Gasoline on hands: Preliminary study on collection and persistence

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Abstract

The identification of an arsonist remains one of the most difficult challenges a fire investigation has to face. Seeking and detection of traces of gasoline could provide a valuable information to link a suspect with an arson scene where gasoline was used to set-up the fire. In this perspective, a first study was undertaken to evaluate a simple, fast and efficient method for collecting gasoline from hands, and to assess its persistence over time.

Four collection means were tested: PVC, PE and Latex gloves, as well as humidified filter paper. A statistical assessment of the results indicates that Latex and PVC gloves worn for about 20 min, as well as paper filter rubbed on hands, allow an efficient collection of gasoline applied to hands. Due to ease of manipulation and to a reduced amount of volatile compounds detected from the matrix, PVC gloves were selected for the second set of experiments.

The evaluation of the persistence of gasoline on hands was then carried out using two initial quantities (500 and 1000 μl). Collection was made with PVC gloves after 0, 30 min, 1, 2 and 4 h, on different volunteers. The results show a common tendency of massive evaporation of gasoline during the first 30 min: a continued but non-linear decrease was observed along different time intervals.

The results of this preliminary study are in agreement with other previous researches conducted on the detection of flammable liquid residues on clothes, shoes and skin.

Generally, the determination of the cause of a fire is a complicated task due to the environment fire investigators have to work in. And once the investigative work has been completed, if arson is suspected or even demonstrated, the investigator is confronted to a subsidiary but not less important challenge: finding evidence of the potential offender. Pieces of evidence such as fingerprints, footprints, DNA, etc., are usually destroyed by the fire, the heat or are covered with soot and their use, even if sometimes possible, is generally precluded [1]. In arson cases, where fire investigators have come to the conclusion that they are dealing with an intentional and criminal act, they often cannot prove who the arsonist is.

Other physical evidence must therefore be looked for on the suspect. At least three types of physical evidence can be found on arsonists. These are ignition implements, such as lighters or matches, burned patterns on skin and hairs or residual accelerants on clothes, shoes or skin [2].

Previous researches conducted by Folkman et al. [3] and Terrapon et al. [4] studied the persistence of gasoline on clothing and shoes. A common finding revealed by these studies is the extremely rapid loss of flammable liquid residues from these items.

Since it is obvious that hands can be soiled when a flammable liquid is deliberately poured on the ground or on furniture, a further study by Almirall et al. [5] proposed a simple fast and inexpensive technique for the detection and identification of ignitable liquid residues on human skin by the use of the solid-phase microextraction (SPME) followed by gas chromatography separation. The proposed technique can be very effective if the SPME sampler is transported to the laboratory after the extraction is conducted in the field as described in that publication. As enlightened by the different studies, a rapid loss of gasoline traces is predicted to occur on human skin. This suggests that a simple technique must be

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applied rapidly by the first police forces attending the fire scene. Such police forces have neither the material nor the knowledge to apply a SPME extraction procedure directly on the site. Then, they must either bring the suspect to the laboratory or call an analyst from the laboratory to the fire scene. In both cases the delay reduces the possibility of collecting and identifying flammable liquid residues and involves some risks of contamination during the transport.

The aim of the present study was then to find a more simple and effective technique that could be easily and quickly applied directly at the fire scene without specialised material or skills.

In this perspective, the present paper evaluates simple methods for collecting gasoline from hands and studies the persistence of gasoline on hands by applying one of them.

1. Materials and methods

The set of experiments was divided into two parts. The first one evaluated four different media for collecting gasoline from hands. In the second part, one of these four collection means was selected and used to study the persistence of gasoline on hands.

For the collection of gasoline, three different types of gloves as well as humidified filter paper were tested:

- polyethylene (PE) gloves (Miobrill, Switzerland), containing no talcum powder;
- latex gloves (Miobrill Finesse, Switzerland), containing no talcum powder;
- polyvinylchloride (PVC) gloves, for medical use, Sensicare™ from Maxxim Medical Inc. (obtained from Merck, Switzerland), containing talcum powder;
- filter paper from Schleicher & Schuell (obtained from Merck, Switzerland), 240 mm diameter.

The gasoline used was lead-free gasoline locally obtained from a Shell petrol station.

1.1. Extraction and analysis of volatile compounds collected on gloves

For both parts of the study, after collection, the gloves or the filter paper were put into Nylon bags (Rilsan type hydrocarbons vapour-proof bags obtained from Romatin AG, St-Margrethen, Switzerland). A passive headspace extraction and concentration of volatile compounds was carried out in an oven at 60 °C for 16 h with a DFLEX™ device (Albrayco Laboratories Inc., Cromwell, USA) composed of a strip of activated charcoal inserted between two semi-permeable membranes and encapsulated in a metal frame [6]. In an attempt to standardise the adsorption conditions on the charcoal strip, a 1 dm³ frame of metallic wire was also placed in the bag to ensure a constant inner volume during all the tests.

The elution of each activated charcoal strip was performed with 800 μl of a 0.5% mixture of 2-hexanone (98% purum, purchased from Aldrich, Switzerland) in carbon disulfide (CS_2, 99.9% purissimum, purchased from Fluka, Switzerland). 2-Hexanone was added as an internal standard to avoid differences in peak response due to variations in manual injections.

1.2. Analytical parameters

Two microliters of the eluent obtained for each sample was analysed by gas chromatography coupled with flame ionisation detection using a Carlo Erba HRGC 5300 Mega Series. The chromatograms and data were plotted on a SIC Chromatocorder 12. The gas chromatograph parameters used for the present study are given in Table 1.

To ensure that the syringe, the injector and the column of the chromatograph were in no way contaminated, a control run containing only carbon disulfide,

Table 1
Gas chromatograph parameters

Column	J & W, DB-5; 30 m; i.d: 0.32 mm; film thickness: 1 μm
Carrier gas	Helium; flow: 2 ml/min
Injector	250 °C (split ratio: 1/50)
Detector	280 °C
Temperature program	
Initial temperature	50 °C
Initial hold	3 min
Ramp rate	5 °C/min
Final temperature	250 °C
Final hold	20 min

from the same batch as the one used for elution, was set up before each sample was analysed.

1.3. Sampling for the evaluation of the different collection media

Before evaluating the efficiency of the different collection media, an analysis of the volatile compounds generated by each of them was carried out using the analytical method described below. The purpose was to evaluate the background noise of the different collection media and identify any risk of interference with the gasoline profile.

In a second stage, the efficiency of the gloves and filter paper as means to collect gasoline was then tested. Using a micro-syringe (Calibra 822 10–100 μl, Socorex, Switzerland), 50 μl of gasoline was placed on the hands of volunteers who then briefly rubbed their hands together. The collection of gasoline was carried out immediately after, at $t = 0$. This was done either by having the subjects wearing the gloves for 20 min, or by swabbing their hands with humidified filter paper; the 20 min time interval was chosen on the basis of previous pilot tests. The gloves or filter paper were immediately put into a nylon bag with a DFLEX™ device, and the bag was sealed and placed in the oven at 60 °C for 16 h. The procedure was applied once on four different volunteers.

1.4. Sampling for the persistence of gasoline on hands

Persistence tests were carried out with only those PVC gloves, that the authors found to be the most appropriate of the tested collection means from the first set of experiments. Three different volunteers participated in these experiments. Two initial quantities of gasoline (500 and 1000 μl) were poured onto their hands with a micro-syringe (Calibra 822 100–1000 μl, Socorex, Switzerland). The collection was made after the volunteers had worn them for different periods of time starting from the moment the gasoline was applied ($t = 0$): at the start, after 30 min, 1, 2 and 4 h. The procedure was repeated with each volunteer for both initial quantities of gasoline and for the different periods of time after application; a total of 30 samples of gloves were obtained.

The experiments in the present paper were carried out with great care to prevent contamination. The gloves were kept in a non-contaminated area and, as noted above, in a vapour-proof bag. The gloves were clearly labelled and used for the purpose of the present study only.

1.5. Identification criteria

The identification of gasoline was based on the ASTM E 1387 standards [7], which state that to conclude in favour of presence of gasoline, a group of four C_3-alkylbenzenes (1-ethyl-3-methylbenzene/1-ethyl-4-methylbenzene,[1] 1,3,5-trimethylbenzene, 1-ethyl-2-methylbenzene and 1,2,4-trimethylbenzene) must be present in addition to other characteristic groups such as C_4-alkylbenzenes and various aliphatic compounds. According to this standard and given the fact

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[1] The peaks of 1-ethyl-3-methylbenzene and 1-ethyl-4-methylbenzene are not always resolved by the gas chromatographic method used for the analysis of volatile compounds of flammable liquids.

Table 2
Target peaks of gasoline selected

C_1-alkylbenzene
  Toluene (A)

C_2-alkylbenzenes
  Ethylbenzene (B)
  meta-Xylene (1,3-dimethylbenzene) and *para*-xylene
    (1,4-dimethylbenzene)[a] (C)
  ortho-Xylene (1,2-dimethylbenzene) (D)

C_3-alkylbenzenes
  Propylbenzene (E)
  1-Ethyl-3-methylbenzene and 1-ethyl-4-methylbenzene[a] (F)
  1,3,5-Trimethylbenzene (G)
  1-Ethyl-2-methylbenzene (H)
  1,2,4-Trimethylbenzene (I)
  1,2,3-Trimethylbenzene (J)

The letters in brackets refer to the labels used in Fig. 4.
  [a] Unresolved peaks (by the applied analytical method).

that only fresh gasoline was used in this study, the criteria for the conclusion of presence of gasoline were extended to the concomitant presence of the 10 peaks given in Table 2.

1.6. Validation of the gas chromatography method

To consider the persistence of gasoline on hands it is necessary to evaluate the quantitative evolution of the initial amount placed on the hands of the volunteer. In order to ensure an accurate evaluation it is necessary to establish, for each compound, that the response of the detector is proportional to the amount of the compound going through it for the whole range of studied concentrations. It is also important to determine the minimal amount significantly detectable under the applied method.

The linearity of the detector response was studied for each of the 10 target peaks over the concentration range 0.01–10% (v/v) of gasoline in the elution mixture (CS_2 with 0.5% (v/v) of 2-hexanone as internal standard). The peak area response to the theoretical detection limit (Y_{LOD}) for each compound of interest was then determined as a signal equal to the blank signal plus three standard deviations of the blank. The extrapolated intercept of the regression lines and the calculated random errors in the values for the slope were used to assess the peak area response to the theoretical limit of detection (Y_{LOD}) for each compound as suggested by Miller and Miller [8].

Fig. 1 shows the linearity of the detector response extrapolated by regression for toluene and ethylbenzene. The calculated peak area response to the theoretical limit of detection (Y_{LOD}) is also indicated.

2. Results

2.1. Background signal of the collection media and risk of interference with gasoline profile

For two of the four collection media tested – PE gloves and Latex gloves – many volatile compounds were detected by the applied extraction and separation methods. The two others – PVC gloves and filter paper – showed no significant background signal other than those of the solvent (CS_2) and its impurities. Fig. 2 presents the volatile patterns obtained for each of the four media and the pattern of the elution solvent (CS_2) alone.

Compared to the chromatographic profile obtained for gasoline, none of the collection media gave any interference. Therefore, based on this consideration, none of them was rejected; experiments on the capacity for collection of the four media were thus carried out.
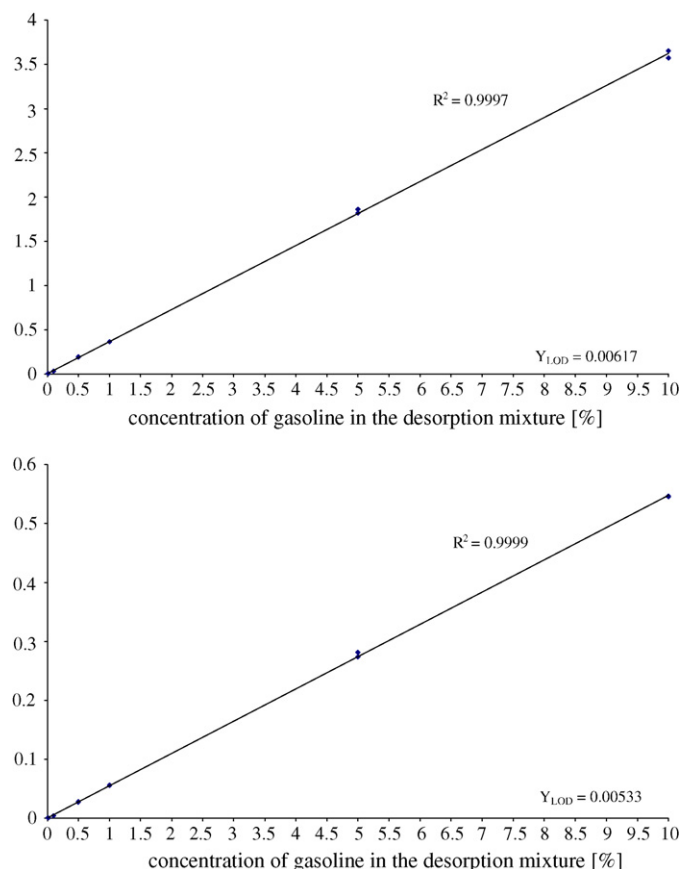

Fig. 1. Example of linear regression obtained for the responses of the detector, for toluene and ethylbenzene, to injections of 2 µl of solution of gasoline in the elution mixture for the following concentration: 0.01%, 0.1%, 0.5%, 1%, 5% and 10%. For each concentration, two samples were analysed (total: 12 analyses for each compound).

2.2. Evaluation of the efficiency of the different collection media

The 10 selected target peaks characteristic of a gasoline profile on the basis of the chosen identification criteria were identified. The ratio of each target peak area to the area of internal standard was calculated. It was observed that there was a certain variation, for a given collection support, of this ratio between the different volunteers, but this variation was not very large. Therefore, the average value of these ratios, for the samples collected for each volunteer, was recorded for the four collection media and the standard deviation was calculated. Fig. 3 shows the results obtained.

A statistical comparison of the results for each collection medium was undertaken assuming that the distribution of the collection efficiencies of the media corresponded to a Gaussian distribution. Considering that all samples were composed of 10 variables, a multivariate statistical evaluation should have been applied but such an approach was precluded by the limited numbers of samples obtained for each collection medium. Therefore, the comparison of the collection efficiencies of the four media was carried out for every one of the 10 target peaks individually. Since the
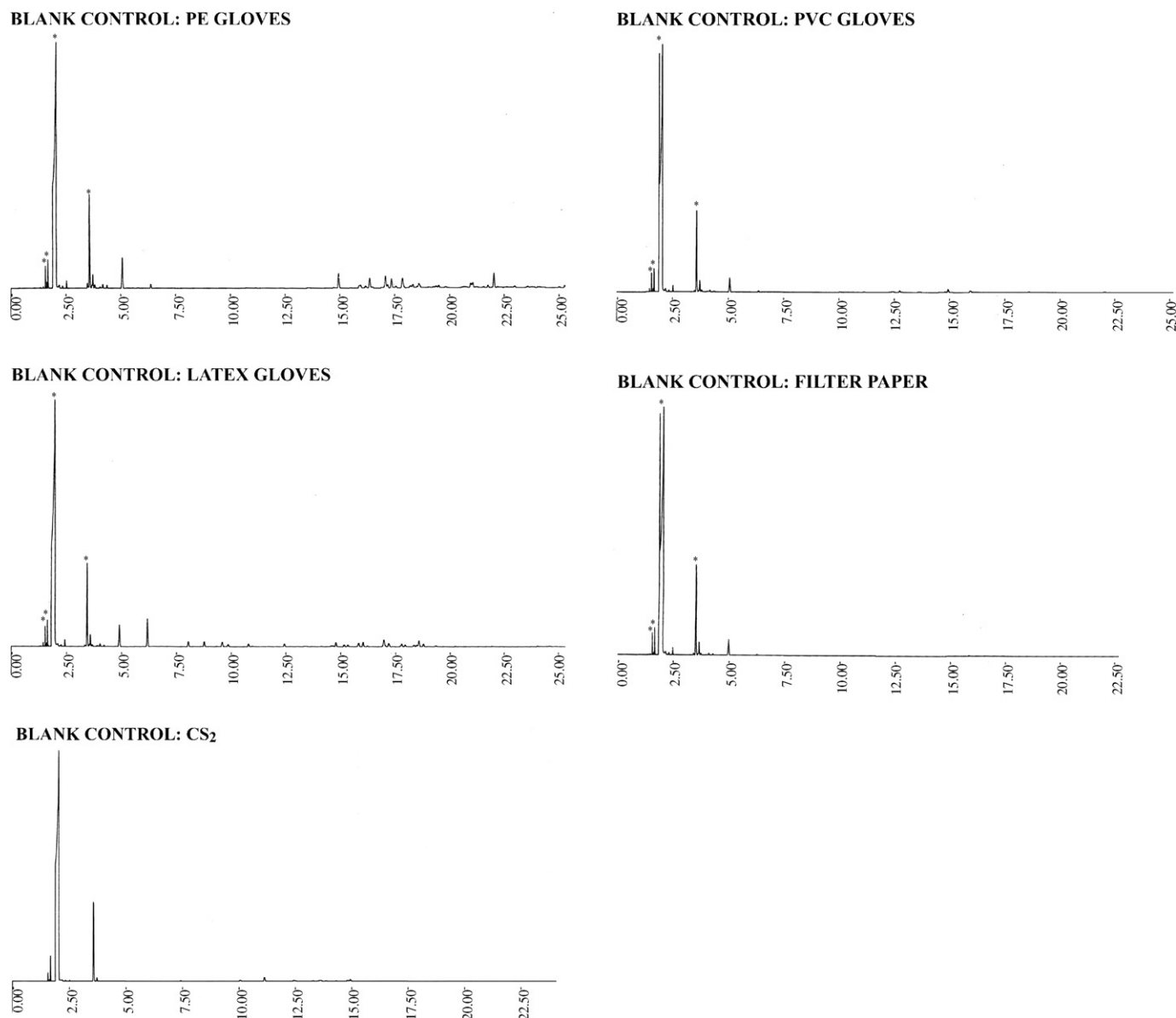
BLANK CONTROL: PE GLOVES

BLANK CONTROL: PVC GLOVES

BLANK CONTROL: LATEX GLOVES

BLANK CONTROL: FILTER PAPER

BLANK CONTROL: CS₂

Fig. 2. Blank controls: patterns obtained for the analysis of the four collection media (top) and for the eluting solvent (CS_2). The symbol * on the four first chromatograms indicates the peaks that correspond to the eluting solvent.

samples analysed for each different medium revealed to have dissimilar variances, the Welch's modification to the Student's *t*-test [9] was applied. This statistical test was selected because it allows a simple and rapid comparison of groups of samples of unequal variances.

Based on a confidence interval of 95%, PE gloves are significantly less efficient in the collection of gasoline than PVC gloves and Latex gloves. No statistically significant difference arises for the other comparisons. Normal variation in human skin accounts for the variations observed in retention, the important variances of the distribution of the results, and the results of the statistical tests.

Therefore, on the basis of statistical considerations, direct comparison of average values, background signal of each tested collection support, as well as ease-of-use, the PVC gloves were selected for the following persistence tests.

2.2.1. Persistence of gasoline on hands

For each volunteer, for both initial amounts of gasoline poured on hands and for each time interval, the area of the 10 target peaks was recorded and normalised to the area of the internal standard. Then the time evolution of the presence of the target peaks was considered.

Independently of the initial amount of gasoline and of the person being tested, the same phenomenon occurs: a considerable loss takes place during the first half-hour. After 30 min, the loss decreases and the residual amount of each target peak recovered tends to stabilise. This phenomenon is shown in Figs. 4 and 5. Fig. 4 presents a series of chromatograms illustrating the evolution of the volatile compounds with time an initial amount of 1000 μl of gasoline; for sake of simplicity, Fig. 5 shows plots of the time persistence for only three of the target peaks,
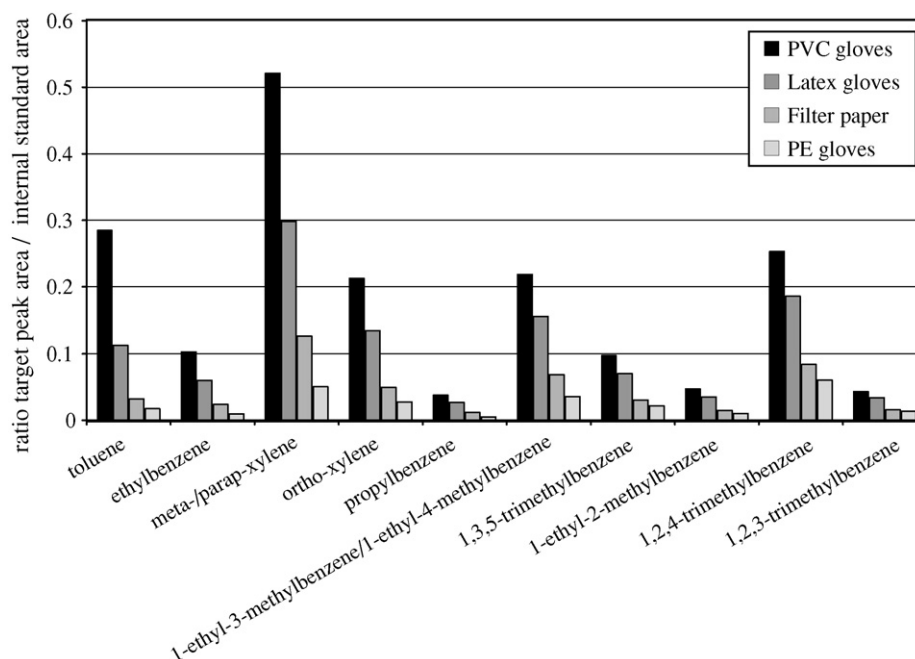
Fig. 3. Ratio of target peak area to internal standard area (average values) for 10 chosen target peaks representing the amount of gasoline collected on the four different media.

but the same phenomenon is recorded for all the 10 target peaks.

The different tests made on the volunteers lead to a recurrent observation in the decreasing rates of the different target peaks: toluene and ethylbenzene seem to decrease at a slower rate than the other components.

This does not correspond to a slower evaporative loss of these two compounds – which would not be logical since they are more volatile than the other compounds considered as targets in this study – but reflects a phenomenon related to the nature of the extraction process of volatiles that was applied; this phenomenon was already covered in previous studies [4,10,11]. The DFLEX^{TM} membrane has a limited collection capacity. Once all the adsorption sites of the membranes are occupied by trapped vapours, a replacement procedure can occur: if the analysed headspace phase is composed of a mixture of vapours of different compounds, even from a same chemical family – as it is the case with gasoline vapours – the lightest compounds tend to be displaced from the membranes by heavier compounds which take their place. This phenomenon occurs because the interaction between activated charcoal and gaseous compounds is stronger with heavier compounds on the same chemical family. This "displacement phenomenon" can occur with all techniques using a passive enrichment of the headspace.

At $t = 0$, when the collection of gasoline is carried out directly after application, the amount of gasoline is sufficient to create a vapour phase exceeding the collection capacity of the DFLEX^{TM} membrane. Thus, for this time interval, the obtained results slightly underestimate the concentration of toluene and ethylbenzene in the headspace in equilibrium with the sample. For the 30 min interval, the amount of gasoline is not sufficient to allow the establishment of this "displacement phenom-

enon", and the quantity of toluene and ethylbenzene collected on the DFLEX^{TM} membrane corresponds to their proportion in the headspace phase. For a qualitative analysis, this phenomenon is not very important, but for quantitative analyses, such as the ones performed to assess the persistence of gasoline on hands, this phenomenon should be carefully considered.

2.2.2. Persistence considering theoretical limits of detection

In order to establish a time interval after which the presence of gasoline could no longer be identified, a comparison was made between the normalised area of each target peak and the peak area response to the theoretical limit of detection calculated for the same target peak. The average values obtained from the measures for the three volunteers were used for this comparison.

For both initial amounts – 500 and 1000 μl – the same boundary was reached. For a collection made directly after application, at $t = 0$, the measured values were above the peak area responses to the limit of detection (Y_{LOD}) for all the target peaks. But due to the extremely rapid loss of gasoline on hands, the detected quantities were below this Y_{LOD} for all the other time steps. Exception were the responses of toluene and 1,2,4-trimethylbenzene, which were just above its Y_{LOD} for an initial amount of 1000 μl and a collection made 30 min after application.

3. Discussion

Although the number of volunteers was limited – only three persons for the persistence tests – the similarity of the average persistence curves for both initial amounts of gasoline and the similarity in range for each volunteer provide a good
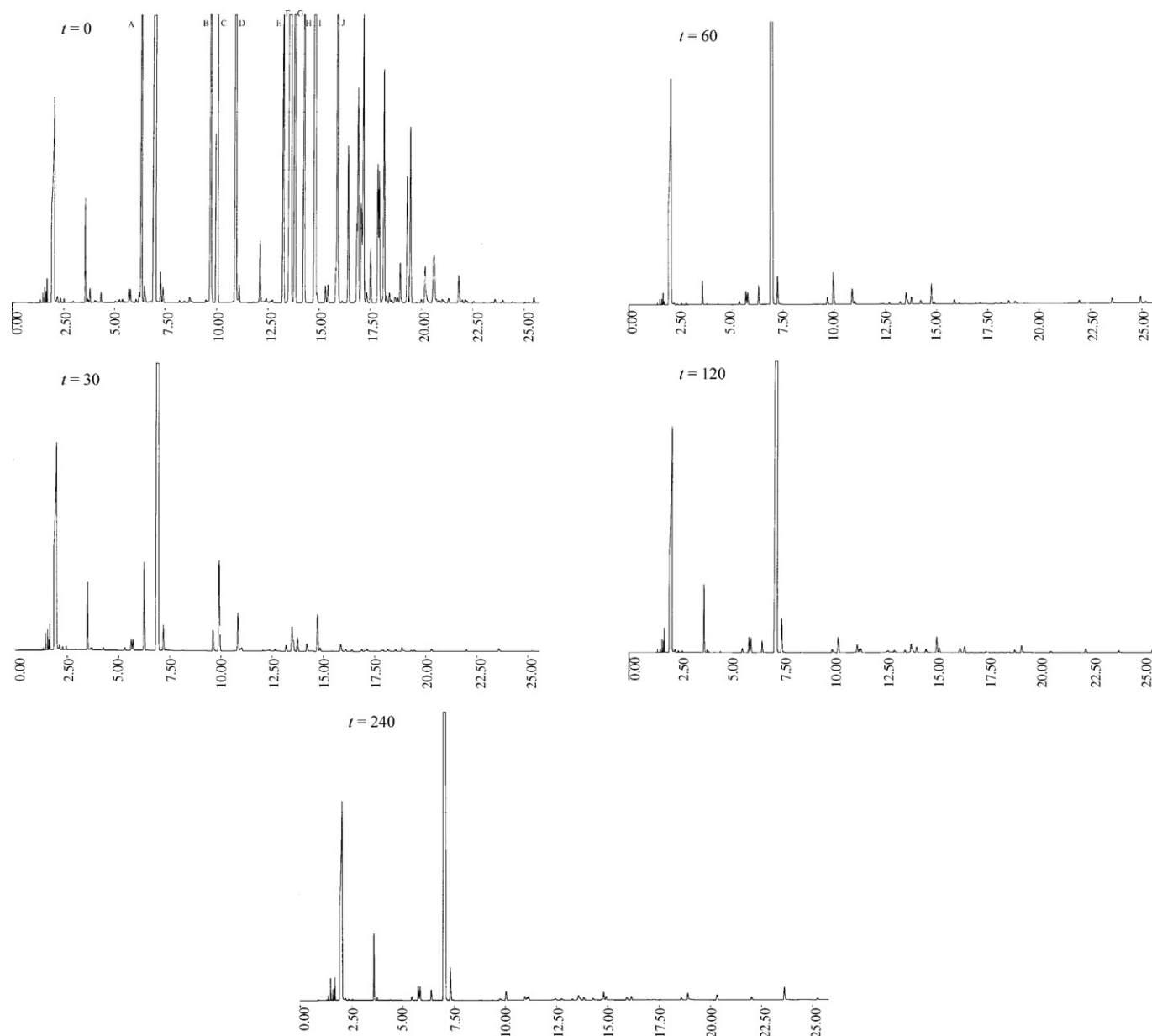
Fig. 4. Series of chromatograms illustrating the recovery of volatiles on the hand of the same person wearing PVC gloves different times after application of 1000 μl of gasoline (top to bottom: *t* = 0, 30, 60, 120 and 240 min). The characters on the first chromatogram refer to the target peaks given previously in Table 2.

indication of the persistence of gasoline on hands. The reader should note that interpretation of the results is considered on the basis of the criteria chosen to calculate the peak area responses to theoretical limits of detection. For example, gasoline traces could still be visually perceived on chromatograms up to 2 h after application for an initial amount of 500 μl and even up to 4 h with 1000 μl. By choosing the conclusion criteria based on Miller and Miller's definition of the peak area response to the theoretical limit of detection [6], a formal identification of gasoline would only be possible in samples collected directly after application for both initial amounts tested. The reader should also be aware that this preliminary study was performed without a previous optimisation of the analytical methodology for traces detection. For instance, the split was fixed at a value of 1 to 50, a compromised ratio used in

routine at the time the research was performed and referring to a screening analysis of samples for a broad range of concentration. There is no doubt that a significant improvement in sensitivity could be achieved by optimizing the analytical parameters for traces detection.

Therefore, the obtained results correspond to a preliminary approach for assessing the collection and persistence of gasoline on hands. It is clear that without further studies any generalisation based on the presented results should be made with great care and clearly states its limits of validity.

Despite a weakness of statistical significance, these results were compared with those of previous studies that evaluated the persistence of gasoline on clothing [2–4]. The same tendencies were observed: in all the studies, an important decrease in quantity occurred during the first half-hour when clothing was
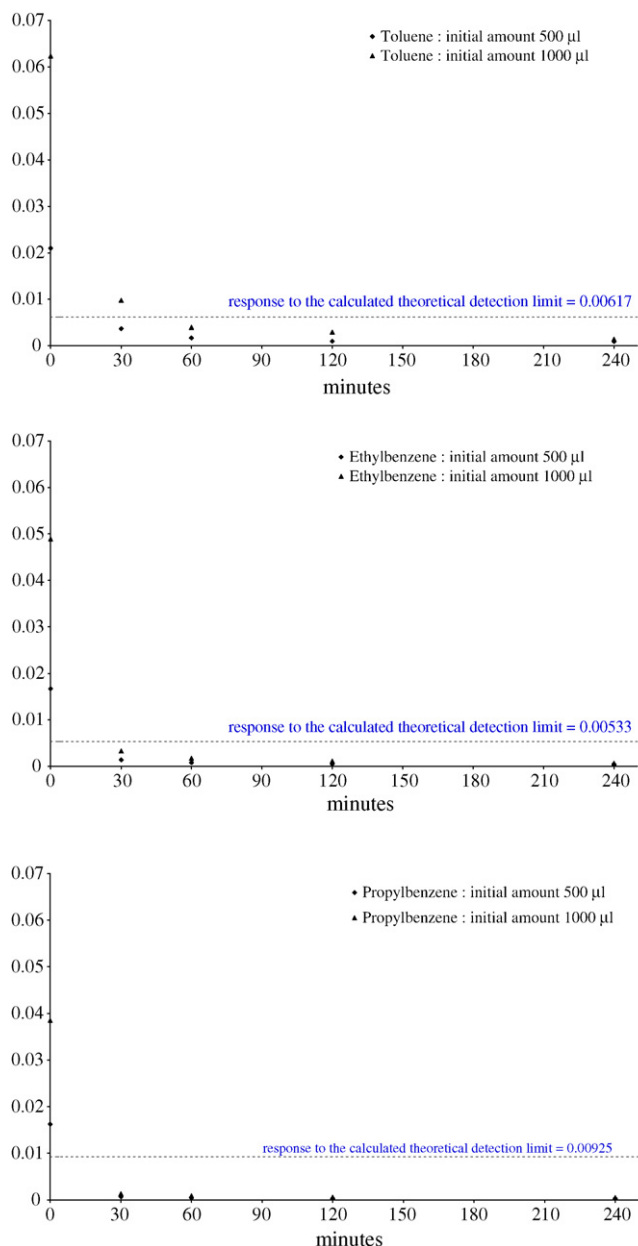
Fig. 5. Decrease of recovery of three selected target peaks – toluene, ethylbenzene and propylbenzene – for both initial amount of gasoline poured on hands of three volunteers (average values).

conditioned at room temperature. This observation supports the trend reported in this work.

In their study, Almirall et al. [5] found that traces of gasoline could not be identified after 75 and 90 min considering ASTM guidelines. Although fundamental differences exist between the study of Almirall et al. and the present research, in terms of sampling, extraction procedures, analytical methodology and conclusion criteria for the detected amount gasoline traces, both studies agree on the fact that collection of gasoline traces on hands is feasible and that it should be done as quickly as possible. In real cases where the proposed methodology was applied, identified gasoline traces were recovered on the hands of suspects many hours after the start of the fire. The reason could be either the presence at a rather large initial amount of gasoline or further contamination from clothes on which liquid residues were splashed.

In this study, the volunteers' occupations were indoors and consisted mainly of office work. It is likely that different occupations or different ambient conditions would have an influence on the persistence of gasoline, shortening or lengthening the period of persistence of gasoline on hands.

Contamination is a concern when applying this technique to actual cases. Two sources of contamination are from the environment and/or contamination from others coming in contact with the suspect. Therefore, the authors recommend to perform a control using an unworn glove stored under same conditions as the gloves used to obtain samples from a suspect. In the same trend to prevent contamination, it is suitable to have someone who has not taken part in the scene investigation to carry out the sampling, for example a non-fire investigator or police officer.

4. Conclusions

The present paper demonstrates that the collection of gasoline on hands is possible and evaluates a simple and rapid method using polymeric gloves. The proposed technique has the major advantage that it can be easily applied by people who do not need to have specific skills or specialised material.

The obtained results indicate that PVC gloves containing talcum powder (Sensicare^{TM} Medical Examination gloves, by Maxxim Medical Inc.) seem to be an accurate collection medium. The gloves should be worn by the suspect for about twenty minutes and then placed in vapour-tight packaging. In the present study, the hydrocarbons were captured by passive adsorption on a DFLEX^{TM} device and the technique was effective.

Gasoline traces were detected up to 2 h after the initial amount of 500 μl was deposited and up to 4 h later when 1000 μl was applied. However, according to the criteria chosen – a detectable quantity above the theoretical peak area response to the limit of detection calculated following Miller and Miller criteria [8] – the presence of gasoline could only be established in samples collected directly after the gasoline was applied.

Leading the perspective opened by this preliminary study, corroborating general findings from previous researches, further work has been undertaken. It should contribute in a near future to enlarge the possibilities of trace evidence exploitation on arsonist's hands.

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